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Annealing of some II-IV-V$_2$ crystals in the vapor of volatile constituents

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ABSTRACT

Experiments on annealing of CdGeAs$_2$- , CdSnAs$_2$- and ZnGeP$_2$-crystals in the vapor of volatile constituents were carried out. Conductivity and Hall effect measurements were performed to characterize the modification of electrical properties, caused by the interaction of the crystal with the gas phase during annealing. Literature data and the results of the present work are discussed based on the results of a quasi-chemical analysis. This yielded that the results of annealing depends essentially on both the conditions of the experiment and the initial imperfection of the crystal. The most probable native structural defects becoming apparent under the annealing were the following: for CdSnAs$_2$ - Sn$_{Cd}$, V$_{As}$; for CdGeAs$_2$ - V$_{As}$, V$_{Cd}$, Cd$_{Ge}$, Ge$_{Cd}$; for CdSiAs$_2$ - Si$_{As}$, V$_{As}$; for CdSiP$_2$ - V$_{Cd}$, V$_P$; for ZnGeP$_2$ - Zn$_{Ge}$, Ge$_{Zn}$, V$_{Zn}$, V$_P$; and for ZnSnP$_2$ - Zn$_{Sn}$, Sn$_{Zn}$, V$_{Zn}$, V$_P$.

INTRODUCTION

There is great interest in the ternary compounds II-IV-V$_2$ (especially CdGeAs$_2$ and ZnGeP$_2$) because of their unique properties, among them their use as NLO converters for mid IR range radiation [1,2]. The widespread practical use of these materials is limited by the presence of absorption bands in their transparency range. These absorption bands are linked to deep level native defects [3-6]. For successful suppression of the undesirable influences of these defects on the properties of the material, it is necessary to define their nature. So far there have not been solutions of this task acceptable to all. Experiments on the influence of annealing in the vapor of volatile components on semiconductor electrophysical parameters may be rather informative in this respect. In this work research of such kind applied to n-CdSnAs$_2$, n- and p-CdGeAs$_2$ and p-ZnGeP$_2$ was fulfilled by the method of "frozen reactions".

EXPERIMENTAL RESULTS

In the case of n-CdSnAs$_2$ the dependence of electron concentrations on vapor pressure appear as curves with a minimum, the depth and position of which on the time axis were defined by defect parameters of the initial sample. This completely agrees with [8]. As it was reported in [9, 10], the hole concentration increased in p-CdGeAs$_2$ with the lapse of time under annealing in As-vapor and went to saturation at a level about p ~ 10^{17} cm^{-3} under annealing times ~ 150 hours. The electron concentration increased in n-CdGeAs$_2$ with the lapse of time under annealing in Cd-vapor and went to saturation at a level about n ~ 10^{18} cm^{-3} under annealing times ~ 100 hours [9]. As to ZnGeP$_2$, it was reported in the work [11] that the hole concentration in the material increased with increase of phosphorus pressure during synthesis

of the compound. According to data of other works, for example, [12-17], annealing in phosphorus vapor reduces the hole concentration (down to p-n conversion of the conductivity type). The results of the present work on annealing in the vapor of volatile components (saturated vapor under pure Cd or As at the temperature of the annealing for $CdGeAs_2$) are presented in Figures 1- 4.
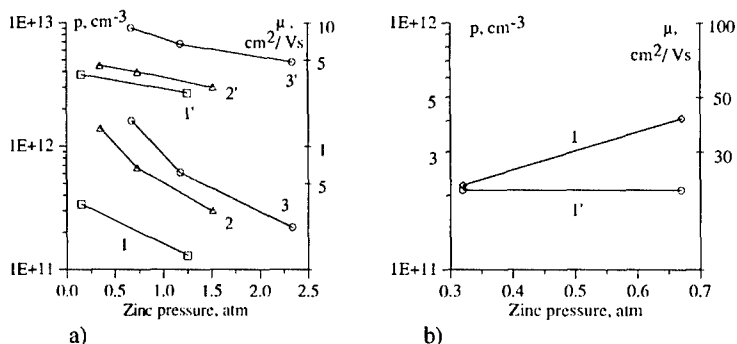

a)   b)

Figure 1. Dependence of concentration (1, 2, 3) and mobility (1', 2', 3') of charge carriers in $ZnGeP_2$ on pressure of Zn; $T_{annealing}$, K: 1-1173; 2-1223; 3-1273; $t_{annealing}$, hours: 1-110; 2-75; 3 - 45; a) material grown from stoichiometric melt under increased P-pressure; b) material grown from a melt containing excess Zn
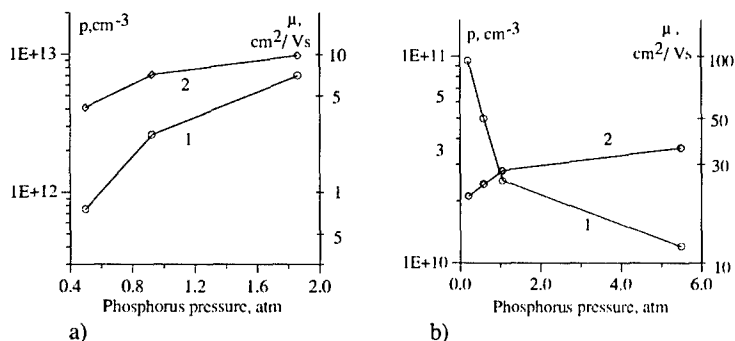

a)   b)

Figure 2. Dependence of concentration (1) and mobility (2) of charge carriers in $ZnGeP_2$ on pressure of phosphorus; $T_{annealing}$ = 1173 K; $t_{annealing}$ =100 hours; a) material grown from stoichiometric melt under increased P-pressure; b) material grown from a melt containing excess Zn
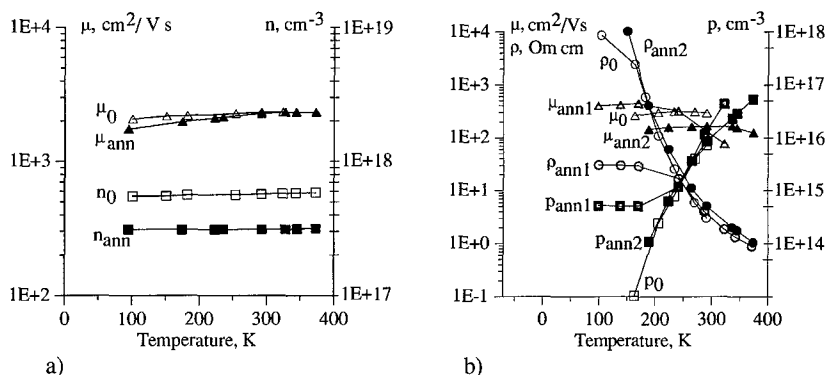
Figure 3. Influence of annealing in As$_4$ on parameters of CdGeAs$_2$; empty symbols - temperature dependence of initial parameters (n$_0$, p$_0$, μ$_0$, ρ$_0$); filled symbols - parameters after annealing at T$_{ann}$ = 773 K; square - concentration, circle - specific resistance, triangle - mobility; a) n-type, t$_{ann}$ =384 hours; b) p-type, t$_{ann1}$ =190 hours, t$_{ann2}$ =384 hours
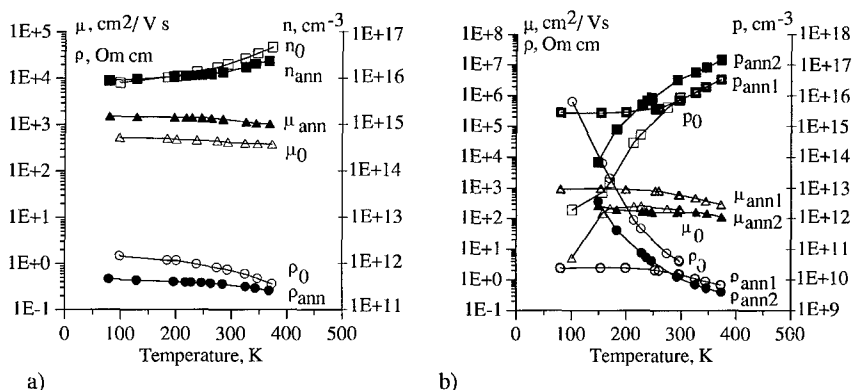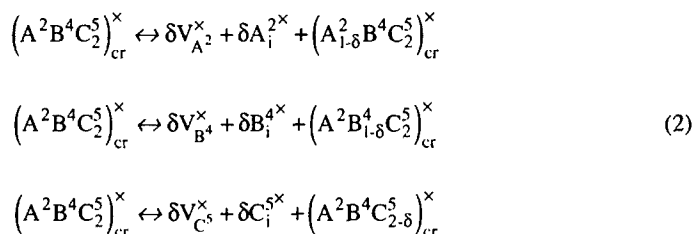
Figure 4. Influence of annealing in cadmium (saturated vapor under pure Cd at 773 K) on electrophysical parameters of CdGeAs$_2$; empty symbols - temperature dependence of initial parameters (n$_0$, p$_0$, μ$_0$, ρ$_0$); filled symbols - temperature dependence of parameters after annealing at T=773 K; square - hole concentration , circle - specific resistance, triangle - hole mobility; a) n-type, t$_{ann}$ =190 hours; b) p-type, t$_{ann1}$ = 30 hours; , t$_{ann2}$ = 90 hours

SCHEME OF QUASI-CHEMICAL ANALYSIS

The processes of formation and interaction of point defects in semiconductors II-IV-V$_2$, and also the processes of interaction of the crystals with a gas phase, may be described as a system of quasi-chemical reactions. The following processes were taken into consideration. Formation of Schottky defects (The Kroger designations [7] are used here and further)
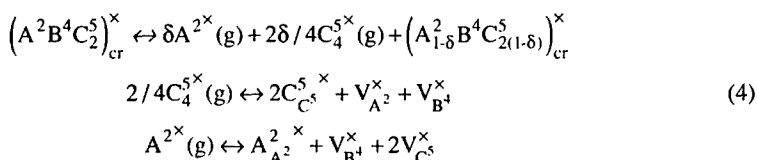
$$0 \leftrightarrow V_{A^2}^{\times} + V_{B^4}^{\times} + 2V_{C^5}^{\times} \tag{1}$$

Formation of Frenkel defects

$$\left(A^2B^4C_2^5\right)_{cr}^{\times} \leftrightarrow \delta V_{A^2}^{\times} + \delta A_i^{2\times} + \left(A_{1-\delta}^2B^4C_2^5\right)_{cr}^{\times}$$

$$\left(A^2B^4C_2^5\right)_{cr}^{\times} \leftrightarrow \delta V_{B^4}^{\times} + \delta B_i^{4\times} + \left(A^2B_{1-\delta}^4C_2^5\right)_{cr}^{\times} \qquad (2)$$

$$\left(A^2B^4C_2^5\right)_{cr}^{\times} \leftrightarrow \delta V_{C^5}^{\times} + \delta C_i^{5\times} + \left(A^2B^4C_{2-\delta}^5\right)_{cr}^{\times}$$

Formation processes of disorder defects in a common form

$$M_{;i}^{\times} + V_{;N}^{\times} \leftrightarrow M_{;N}^{\times} \qquad (3)$$

Interaction processes of crystals with a gas phase using the non-volatility of the elements B^4 (Si, Ge and Sn) approximation

$$\left(A^2B^4C_2^5\right)_{cr}^{\times} \leftrightarrow \delta A^{2\times}(g) + 2\delta/4C_4^{5\times}(g) + \left(A_{1-\delta}^2B^4C_{2(1-\delta)}^5\right)_{cr}^{\times}$$

$$2/4C_4^{5\times}(g) \leftrightarrow 2C_{C^5}^{5\,\times} + V_{A^2}^{\times} + V_{B^4}^{\times} \qquad (4)$$

$$A^{2\times}(g) \leftrightarrow A_{A^2}^{2\,\times} + V_{B^4}^{\times} + 2V_{C^5}^{\times}$$

Applying the law of mass action to the quasi-chemical reactions and solving the obtained set of equations with respect to concentration of a given point defect under a choice of vapor pressure of one of the volatile components p_{A^2} or $p_{C_4^5}$ as an independent variable (for temperatures at which component C^5 exists mainly as four-atom molecules in a gas phase) yields the following expressions

$$[N_i^{\times}] = K_{i1}\left(p_{C_4^5}\right)^{\alpha_i} \quad \text{and} \quad [N_i^{\times}] = K_{i2}\left(p_{A^2}\right)^{\beta_i}, \qquad (5)$$

where $[N_i^{\times}]$ is the concentration of neutral defects of i-type, $K_{i1,2}$ are constants at a given temperature, α_i, β_i are constants from the table I

Table I. Exponents α_i or β_i in dependencies of concentrations of neutral native point defects in semiconductors upon pressure of volatile components p_{A^2} or $p_{C_4^5}$ respectively

$[N_i^{\times}]$	$V_{A^2}^{\times}$	$V_{B^4}^{\times}$	$V_{C^5}^{\times}$	$A_i^{2\times}$	$B_i^{4\times}$	$C_i^{5\times}$	$A_{B^4}^{2\,\times}$	$A_{C^5}^{2\,\times}$	$B_{C^5}^{4\,\times}$	$B_{A^2}^{4\,\times}$	$C_{A^2}^{5\,\times}$	$C_{B^4}^{5\,\times}$
α_i	1/2	0	-1/4	-1/2	0	1/4	-1/2	-3/4	-1/4	1/2	3/4	1/4
β_i	-1	0	1/2	1	0	-1/2	1	3/2	1/2	-1	-3/2	-1/2

Applying the law of mass action to the quasi-chemical reactions of ionization of neutral native point defects of the type

$$A_1^{\times} \leftrightarrow A_1^{'} + h^{\cdot} \ \text{ or } \ D_1^{\times} \leftrightarrow D_1^{\cdot} + e^{'} \tag{6}$$

yields a set of equations

$$
\begin{array}{ll}
1.\ V_{A^2}^{'} \cdot p = K_1 \cdot V_{A^2}^{\times} & \quad 7.\ A_{B^4}^{2\,'} \cdot p = K_7 \cdot A_{B^4}^{2\ \times} \\[2mm]
2.\ V_{B^4}^{'} \cdot p = K_2 \cdot V_{B^4}^{\times} & \quad 8.\ A_{C^5}^{2\,'} \cdot p = K_8 \cdot A_{C^5}^{2\ \times} \\[2mm]
3.\ V_{C^5}^{'} \cdot n = K_3 \cdot V_{C^5}^{\times} & \quad 9.\ B_{C^5}^{4\,'} \cdot p = K_9 \cdot B_{C^5}^{4\ \times} \\[2mm]
4.\ A_i^{2\,'} \cdot n = K_4 \cdot A_i^{2\times} & \quad 10.\ B_{A^2}^{4\ '} \cdot n = K_{10} \cdot B_{A^2}^{4\ \times} \\[2mm]
5.\ B_i^{4\,'} \cdot n = K_5 \cdot B_i^{4\times} & \quad 11.\ C_{A^2}^{5\ '} \cdot n = K_{11} \cdot C_{A^2}^{5\ \times} \\[2mm]
6.\ C_i^{5\,'} \cdot p = K_6 \cdot C_i^{5\times} & \quad 12.\ C_{B^4}^{5\ '} \cdot n = K_{12} \cdot C_{B^4}^{5\ \times}
\end{array}
\tag{7}
$$

Adding to the given system written in a common form as

$$A_1^{'} \cdot p = K_1 \cdot A_1^{\times} \ \text{ or } \ D_1^{\cdot} \cdot n = K_1 \cdot D_1^{\times},$$

the equation for equilibrium concentration of electrons and holes

$$n \cdot p = K_{14},$$

and also the equation of an electroneutrality

$$V_{A^2}^{'} + V_{B^4}^{'} + C_i^{5\,'} + A_{B^4}^{2\,'} + A_{B^4}^{2\,'} + B_{C^5}^{4\,'} + n = V_{C^5}^{\cdot} + A_i^{2\cdot} + B_i^{4\cdot} + B_{A^2}^{4\ \cdot} + C_{A^2}^{5\ \cdot} + C_{B^4}^{5\ \cdot} + p,$$

and solving the obtained system with respect to concentration of free charge carriers using data from table I, we obtain dependencies of free electron concentration (free hole concentration) upon pressure of volatile components, such as (8) and (9).

$$n^2 = \frac{K_3' p_{C_4}^{-1/4} + K_4' p_{C_4}^{-1/2} + K_5' + K_{10}' p_{C_4}^{1/2} + K_{11}' p_{C_4}^{3/4} + K_{12}' p_{C_4}^{1/4} + K_{14}}{K_1'' p_{C_4}^{1/2} + K_2'' + K_6'' p_{C_4}^{1/4} + K_7'' p_{C_4}^{-1/2} + K_8'' p_{C_4}^{-3/4} + K_9'' p_{C_4}^{-1/4} + 1}, \tag{8}$$

where $K_l' = K_l \cdot K_i$, $K_l'' = K_l \cdot K_i / K_{14}$, K_i from (5).

$$p^2 = \frac{K_1'' p_{C_5}^{1/2} + K_2'' + K_6'' p_{C_5}^{1/4} + K_7'' p_{C_4}^{-1/2} + K_8'' p_{C_4}^{-3/4} + K_9'' p_{C_4}^{-1/4} + K_{14}^2}{K_3' p_{C_5}^{-1/4} + K_4' p_{C_4}^{-1/2} + K_5' + K_{10}' p_{C_5}^{1/2} + K_{11}' p_{C_4}^{3/4} + K_{12}' p_{C_4}^{1/4} + K_{14}}, \tag{9}$$

where $K_l' = K_l \cdot K_i$, $K_l'' = K_l \cdot K_i \cdot K_{14}$, K_i from (5).

Analysis of the obtained dependencies of the equilibrium concentration of free charge carriers on pressure yields the following conclusions:
Increase of pressure of the component C^5 in a system leads to
a) increase in concentration of the donors, connected with disorder, that is B_A, C_A, C_B;

b) decrease in concentration of the donors, connected with vacancies of an anion and intersti-
tial cations, that is V_C, A_i;

c) increase in concentration of acceptors, connected with vacancies in the cation sublattice and
interstitial anions, that is V_A, C_i;

d) decrease in concentration of acceptors, connected with disorder, that is A_B, A_C, B_C.

Therefore, it is most probable that the experimentally observed (for example, from measure-
ments of the Hall effect on samples after annealing under high pressure of one of the volatile
constituents) shift of carrier concentration in the direction of n-type conductivity with a simul-
taneous decrease in mobility corresponds to the situation a); the experimentally observed shift
of carrier concentration in the direction of p-type conductivity with a simultaneous increase in
mobility corresponds to the situation b); the shift in carrier concentration in the direction of p-
type with a simultaneous decrease of mobility corresponds to the situation c); the shift in car-
rier concentration in the direction of n-type with a simultaneous increase of mobility corre-
sponds to the situation d).   Designating by ↑, the increase in defect concentration and by ↓,
the decrease in defect concentration, the results of the analysis may be presented as the follow-
ing schemes:

Table II. The scheme of the correspondence of experimentally observed shift of charge carri-
ers concentration and mobility (a case of primary ion scattering) to a change of concentration
of native structural defects after annealing under high pressure of C^5 or A^2

Annealing under high pressure of	Observation	Possible cause	Concrete definition
C^5	n↑ p↓ μ↑	A↓	A_B↓, A_C↓, B_C↓
C^5	n↑ p↓ μ↓	D↑	B_A↑, C_A↑, C_B↑
C^5	n↓ p↑ μ↑	D↓	V_C↓, A_i↓
C^5	n↓ p↑ μ↓	A↑	V_A↑, C_i↑
A^2	n↑ p↓ μ↑	A↓	V_A↓, C_i↓
A^2	n↑ p↓ μ↓	D↑	V_C↑, A_i↑
A^2	n↓ p↑ μ↑	D↓	B_A↓, C_A↓, C_B↓
A^2	n↓ p↑ μ↓	A↑	A_B↑, A_C↑, B_C↑

QUASI-CHEMICAL ANALYSIS OF EXPERIMENTAL DATA

The results of a change in electrophysical parameters under the heat treatment of some II-
IV-V_2 crystals in the vapor of volatile constituents, obtained in the present work and taken
from the literature, are analyzed by correlating the experimentally observed shift of charge car-
rier concentration and mobility (a case of primary ion scattering) to a change of concentration
in native structural defects after annealing under high pressure of C^5 or A^2 from table III. The
results of the analysis are given in tables III and IV.

For CdSnAs$_2$ the presence of two types of donors results from the existence of two time-
stages of annealing in vapor of the both volatile components. The first annealing time-stage of
n-CdSnAs$_2$ (decrease of electron concentration with sharp increase of electron mobility during
annealing in As-vapor) is defined as a fast processes, (for instance, corresponding to the equa-
tions 3, 4 of system (7)) and connected mainly with the decrease in concentration of donor va-
cancies [V_{As}]. The second stage changes (increase of electron concentration during annealing
in As-vapor) are affected by competitive slower processes (for instance, corresponding to the
equations 10 - 12 of system (7)), connected with modifications of disorder defect concentra-
tion. Under annealing in Cd-vapor the stages traded places.

Literature data and the results of the present work concerning $ZnGeP_2$ testify that the conditions of the chemical and thermal history of $ZnGeP_2$ crystals (chemical composition of a melt, composition and pressure in a growth technological system etc.) have much influence on concentrations of native structural defects and, because of that, on properties and behavior of $ZnGeP_2$ under further treatments. As follows from figures 1, 2 and from the analysis the crystals $ZnGeP_2$ with different "previous history" have a different ensemble of native structural defects and react differently on an annealing in vapor of volatile components.

For $ZnGeP_2$,the presence of both vacancies (in the present work for $ZnGeP_2 < P>$, when $[V_P]$, probably less than equilibrium concentration for conditions of annealing in Zn-vapor) and disorder defects in the cation sublattice (in the present work for $ZnGeP_2 < Zn>$) were observed.

For $CdGeAs_2$ the presence of at least two native acceptors has been observed in experiments utilizing radiation damage, magnetic resonance and thermal admittance spectroscopy [20]. As follows from Figures 3, 4 the annealing of n-$CdGeAs_2$, in both As atmosphere and Cd atmosphere, yielded a diminution of electron concentration. In the first case it was accompanied by a diminution of mobility (μ), in the second case it was accompanied by magnification of μ. In the approximation of the scheme used in table I, it corresponds to 1) magnification of concentration V_{Cd} (and, probably, As_i), 2) diminution of concentration of disorder defects such as Ge_{Cd}. We note that annealing in Cd vapor, carried out by the authors of work [9], on n-$CdGeAs_2$ at $T_{anneal} = 400$ °C, led to (from $\sim 2 \cdot 10^{16}$ cm^{-3} to $\sim 8 \cdot 10^{17}$ cm^{-3}) the increase in the electron concentration. Probably, the less than 100 °C annealing temperature in experiment [9] was the reason for the smaller activity of disorder defects. The annealing processes were defined by an extreme modification of the concentration of vacancies and led to a sharp increase in electron concentration due to a lack of a competing process, giving an opposite outcome. In the annealing of p-$CdGeAs_2$, a simultaneous course of several competing processes is also observed. The initial annealing stage (30 hours in As_4 vapour) gave p-n conversion of conductivity of samples under study (from p $\sim 7 \cdot 10^{15}$ cm^{-3} , $\mu \sim 290$ cm^2/V·s to n $\sim 8 \cdot 10^{15}$ cm^{-3}, $\mu \sim 2800$ cm^2/V·s at $T_{meas} \sim 290$ K ,and n $\sim 5 \cdot 10^{15}$ cm^{-3}, $\mu \sim 3900$ cm^2/V·s at $T_{meas} \sim 95$ K). Using the same approximations as in table I, the concentration of disorder defects ($Cd_{Ge} \downarrow$, $Ge_{Cd} \uparrow$) increases, or it is explained by uncontrollable doping of the samples (for example, by O_2). The outcomes of long annealing of p-$CdGeAs_2$ in As_4 are presented in figure 3 b). The increase in hole concentration with respective change in mobility corresponds to a stage of 190 hours of annealing. It can be described by the increase of $[V_{Cd}]$ and the decrease of $[V_{As}]$. The stage of 384 hours is characterized by an outcome (p $\downarrow$, $\mu \downarrow$). That can mean a prevalence of the first process ($Ge_{Cd} \uparrow$). Similar experiments on annealing of p-$CdGeAs_2$ in As_4 vapor were carried out by the authors [9, 10]. In this case the annealing temperature differed less (450 °C [10] and 520 °C [9]). However, the influence of the process, defined by disorder defects, which were observed in the work [9, 10] are lacking. Probably, it is possible to assume, that in this case the initial imperfection of samples under study plays a key role. A different imperfection caused different routes and different times, necessary for reaching an equilibrium condition. From an analysis of the observed modifications of electrophysical parameters, associated with annealing of p-$CdGeAs_2$ in Cd, we can approximate the influence of processes connected with disorder defects as follows. Such processes as $A_B \uparrow$, $A_C \uparrow$, $B_C \uparrow$ and $B_A \downarrow$, $C_A \downarrow$, $C_B \downarrow$ play a defining role. Thus, after annealing of n- and p-$CdGeAs_2$ under high pressure of the volatile components, we observed the influence of such native defects as V_{Cd}, V_{As}, Cd_{Ge}, Ge_{Cd}. We note that annealing in the vapor of the element A^2 (Cd) was difficult because of the high chemical activity of the element A^2 in relation to a surface of crystals $A^2B^4C^5_{;2}$. This caused formation of surface layers of a different chemical nature.

Table III. The results of the quasi-chemical analysis of experimental data of the present work and also literary data on annealing in vapour of volatile components for some II-IV-V$_2$ (The data of the present work are marked by an asterisk)

Compound	Annealing in vapour	Observed change	Responsible native defects
CdSnAs$_2$	C^5	1) n↓ p↑ μ↑ [8],[*]	V$_C$↓, A$_i$↓
	C^5	2) n↑ p↓ μ↓ [8],[*]	B$_A$↑, C$_A$↑, C$_B$↑
	A^2	1) n↓ p↑ μ↑ [8],[*]	B$_A$↓, C$_A$↓, C$_B$↓
	A^2	2) n↑ p↓ μ↓ [8],[*]	V$_C$↑, A$_i$↑
CdGeAs$_2$	C^5	1) n↓ p↑ μ↑ [10, 9],[*]	V$_C$↓, A$_i$↓
	C^5	2) n↓ p↑ μ↓ [*]	V$_A$↑, C$_i$↑
	C^5	3) n↑ p↓ μ? [*]	A$_B$↓, A$_C$↓, B$_C$↓ B$_A$↑, C$_A$↑, C$_B$↑
	A^2	1) n↑ p↓ μ? [10], [*]	V$_C$↑, A$_i$↑ or V$_A$↓, C$_i$↓
	A^2	2) n↓ p↑ μ↑ [*]	B$_A$↓, C$_A$↓, C$_B$↓
	A^2	3) n↓ p↑ μ↓ [*]	A$_B$↑, A$_C$↑, B$_C$↑
CdSiAs$_2$	C^5	1) n↓ p↑ μ↑ [11,18]	V$_C$↓, A$_i$↓
	C^5	2) n↑ p↓ μ↑ [11]	A$_B$↓, A$_C$↓, B$_C$↓
	A^2	1) n↑ p↓ μ↓ [11,18]	V$_C$↑, A$_i$↑
	A^2	2) n↓ p↑ μ↓ [11]	A$_B$↑, A$_C$↑, B$_C$↑
CdSiP$_2$	C^5	n↓ p↑ μ? [15]	V$_C$↑, A$_i$↑, V$_A$↓, C$_i$↓
ZnGeP$_2$	C^5	n↓ p↑ μ? [11]	V$_C$↑, A$_i$↑, V$_A$↓, C$_i$↓
	A^2	n↓ p↑ μ↑ [12]	B$_A$↓, C$_A$↓, C$_B$↓
	C^5	n↑ p↓ μ↑ [12]	A$_B$↓, A$_C$↓, B$_C$↓
	A^2	n↓ p↑ μ? [13-17]	disorder defects
	C^5	n↑ p↓ μ? [13-17]	disorder defects
ZnGeP$_2$<P>	A^2	n↑ p↓ μ↓ [*]	V$_C$↑, A$_i$↑
	C^5	n↓ p↑ μ↑ [*]	V$_C$↓, A$_i$↓
ZnGeP$_2$<Zn>	A^2	n↓ p↑ μ↓ [*]	A$_B$↑, A$_C$↑, B$_C$↑
	C^5	n↑ p↓ μ↑ [*]	A$_B$↓, A$_C$↓, B$_C$↓
ZnSnP$_2$	A^2	1) n↓ p↑ μ↑ [19]	B$_A$↓, C$_A$↓, C$_B$↓
	A^2	2) n↑ p↓ μ↓ [19]	V$_C$↑, A$_i$↑
	C^5	1) n↑ p↓ μ↑ [19]	A$_B$↓, A$_C$↓, B$_C$↓
	C^5	2) n↓ p↑ μ↓ [19]	V$_A$↑, C$_i$↑

Table IV. The most probable native structural defects in some A^{2}B^{4}C$^5_2$ exhibited under heat treatment in vapor of volatile constituents and satisfying to the Hume-Rothery criterion

Compound	CdSnAs$_2$	CdGeAs$_2$	CdSiAs$_2$	CdSiP$_2$	ZnGeP$_2$	ZnSnP$_2$
Defects	Sn$_{Cd}$, V$_{As}$	V$_{As}$, V$_{Cd}$, Cd$_{Ge}$, Ge$_{Cd}$	Si$_{As}$, V$_{As}$	V$_{Cd}$, V$_P$	Zn$_{Ge}$, Ge$_{Zn}$, V$_{Zn}$, V$_P$	Zn$_{Sn}$, Zn$_P$, Sn$_{Zn}$, P$_{Zn}$, V$_{Zn}$, V$_P$

CONCLUSIONS

1. Experiments on annealing of $CdGeAs_2$-, $CdSnAs_2$- and $ZnGeP_2$-crystals in the vapor of volatile constituents were carried out. Conductivity and Hall effect measurements were performed to characterize the modification of electrical properties, caused by interaction of the crystal with the gas phase during the annealing.

2. A scheme for correlating the experimentally observed shifts of charge carrier concentration and mobility (a case of primary ion scattering) to a change in concentration of native structural defects after annealing under high pressure of C^5 or A^2, based on quasi-chemical analyses was presented.

3. The literature data and results of the present work on the annealing were discussed based on the results of a quasi-chemical analysis.

4. It was noted that the outcomes of the annealing essentially depend on both the initial imperfections of the crystal and the conditions of the experiment as they define the route and time of reaching an equilibrium..

5. For some $II-IV-V_2$ the most probable native structural defects becoming apparent under heat treatment in the vapor of volatile constituents and satisfying to the Hume-Rothery criterion were the following: For $CdSnAs_2$ - Sn_{Cd}, V_{As}; for $CdGeAs_2$ - V_{As}, V_{Cd}, Cd_{Ge}, Ge_{Cd}; for $CdSiAs_2$ - Si_{As}, V_{As}; for $CdSiP_2$ - V_{Cd}, V_P; for $ZnGeP_2$ - Zn_{Ge}, Ge_{Zn}, V_{Zn}, V_P; for $ZnSnP_2$- Zn_{Sn}, Sn_{Zn}, V_{Zn}, V_P.-

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